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ELECTROCHEMICAL STUDIES IN THE SYNTHESIS OF N-F COMPOUNDS

Contract No. Nonr-4054(00)
Research Project No. RR001-06-02
ARPA Order No. 399, Program Code No. 2910

November 11, 1964

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TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

Abstract

The work during this past quarter was devoted primarily to studying the anodic polarization of Monel in anhydrous hydrogen fluoride (AHF) and to the electrolysis of ammonium fluoride (NH_4F) in AHF using Monel as the working electrode. Conductance studies were also performed to determine the rate of contamination of the AHF as it was held in the sealed cells. Determinations of the effects of electrolysis and additions of water and NH_4F on the conductivity of HF were also made.

Pyrolytic carbon was investigated as a possible electrode material. The carbon was mounted in Kel-F to expose only a single crystal plane, and, although it resisted attack by AHF, it disintegrated when fluorine was evolved anodically.

Results to date indicate that fluorination during the electrolysis of NH_4F in AHF proceeds by chemical rather than by an electrochemical mechanism.

ELECTROCHEMICAL STUDIES IN THE SYNTHESIS OF N-F COMPOUNDS

I. INTRODUCTION

The objective of this work is to employ electrochemical techniques to determine if the fluorination of ammonium and hydrazinium salts proceeds by a stepwide mechanism or if F is substituted for H in a random fashion.

During the past quarter Monel has been used as a working electrode to study the electrolysis of NH_4F in AHF. Monel will also be used to study the electrolysis of N_2H_5F in future work.

Monel is the best material used to date in regard to corrosion; however, its behavior on anodic polarization is not yet understood. During the last quarter polarization, cathodic stripping, and conductivity experiments were performed to clarify the processes which take place on Monel. Since anodic polarization in HF solutions of NH_4F involves fluorine evolution, electrode oxidation, fluorination of NH_4^+, and contaminant oxidation, it is important that the contribution of each be understood and evaluated for adequate interpretation of the results obtained.

II. EXPERIMENTAL APPARATUS

Several improvements were made in the experimental apparatus during the last quarter for the following purposes:

1. Some metal (Monel) parts in the HF handling system were replaced with Kel-F parts to lessen contamination of the HF during transfer to the electrolysis cells.

2. The electrolysis cells were modified to facilitate disassembly, cleaning, and experimental operation. Kel-F was used for construction of the cell bodies.

3. Design of the Hg/Hg_2F_2 electrode was changed to permit changing or inspection of the electrode when the cell is filled with HF.

4. Additional procedures were added to improve and maintain purity of the HF in the experimental cells. These consisted of fluorinating the cells before filling and pre-electrolyzing the HF <u>in situ</u> with a pair of nickel electrodes. Purity of the HF in the cells is checked frequently by conductivity measurements with platinum electrodes.

Figure 1 shows the experimental cells in various stages of assembly and in final assembly in a protective dry box. The cylindrical dry boxes are constructed from Plexiglas and contain silica gel to prevent condensation of moisture on the electrode terminals. It is necessary to exclude moisture from the cell to prevent spurious signals to the high-impedance measuring equipment used.

A schematic diagram of the arrangement of the electrodes in the cell is shown in Figure 2. In operation, the cleaned, dried cell is assembled with all electrodes in place except the working and reference electrodes. The cell is then treated with fluorine gas, purged with dry nitrogen, and filled with hydrogen fluoride from the NaF trap. The HF is then electrolyzed with the nickel screen electrodes, while bubbling dry N_2, until a high

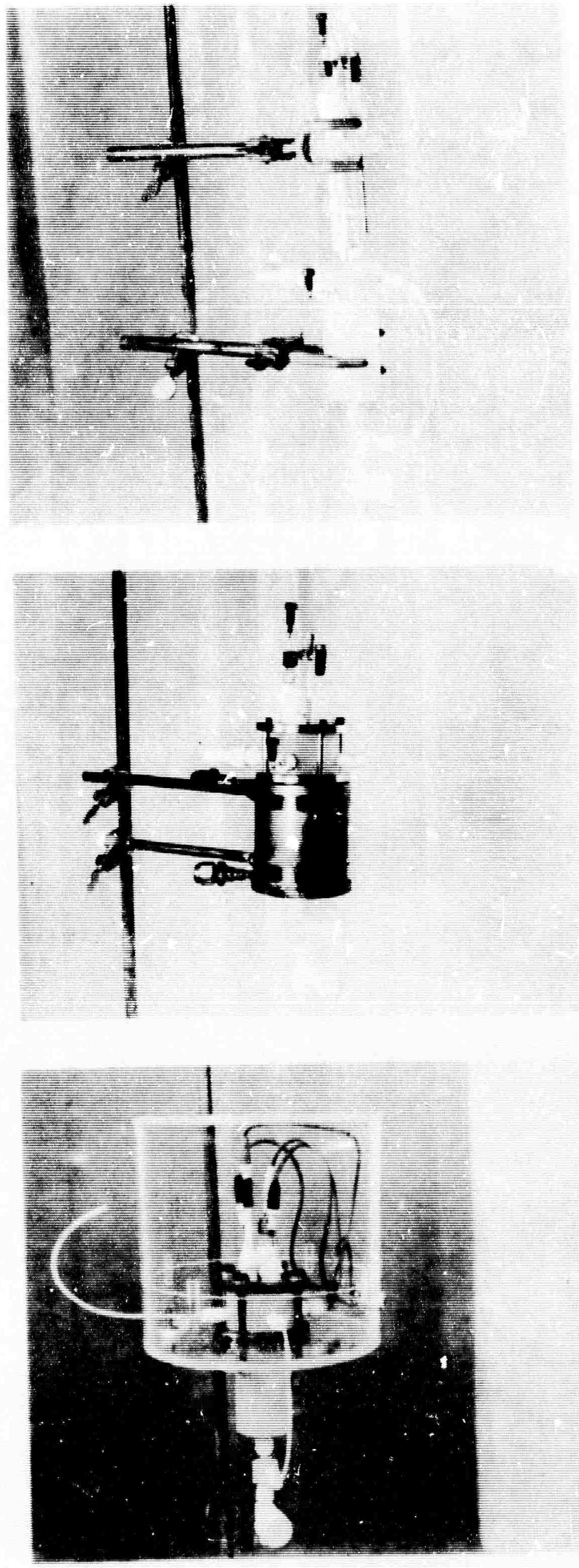

Fig. 1- ASSEMBLED CELL AND DRY BOX

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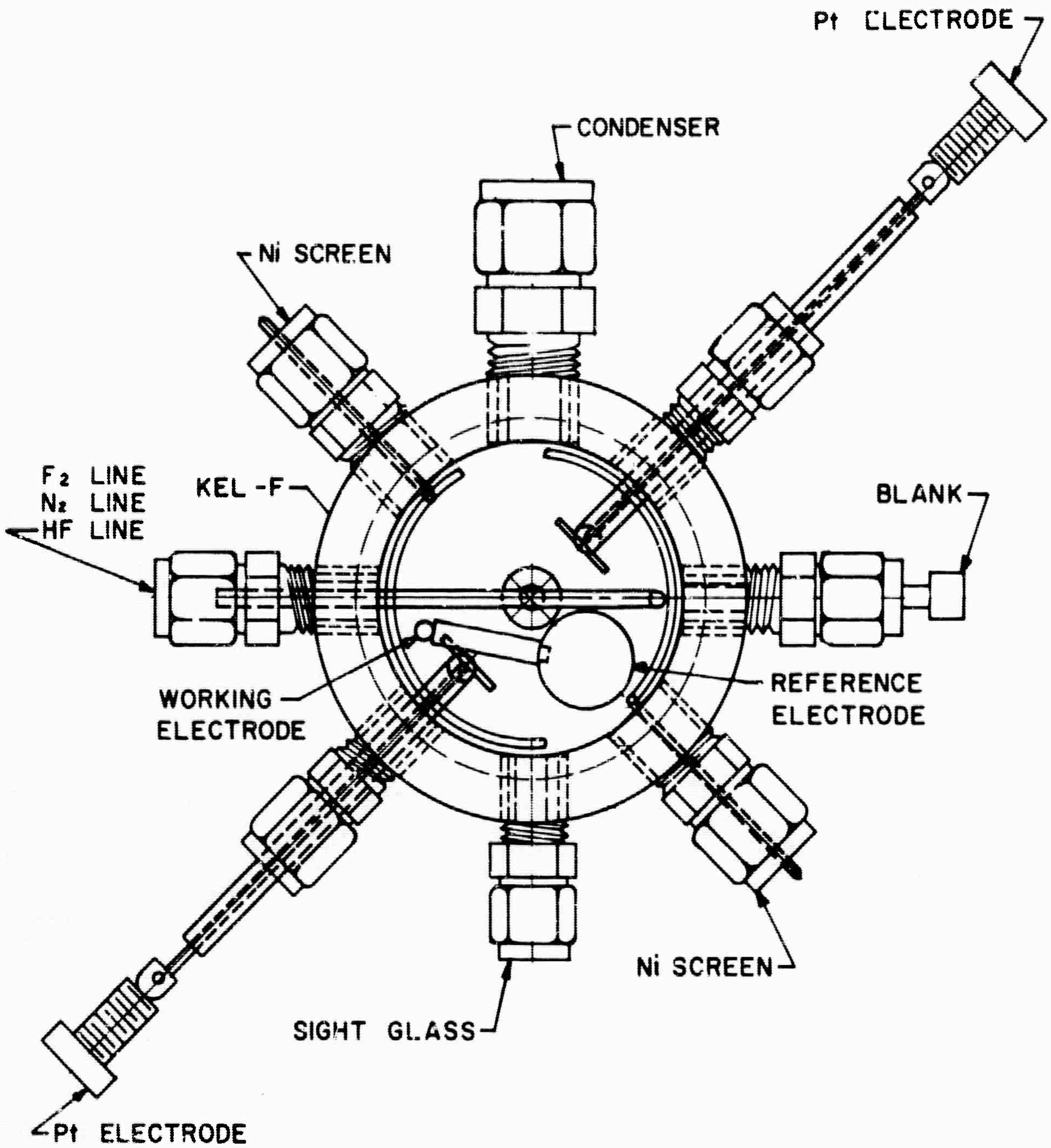

Fig. 2-ELECTROLYTIC CELL BODY TOP VIEW

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resistivity is obtained as shown by measurements with the platinum electrodes. The working and reference electrodes are then introduced for performance of the electrochemical experiments.

Configuration of the reference electrode is shown in Figure 3. The sheath which forms the solution bridge is always in place in the cell; however, the inner part containing the Hg/Hg_2F_2 electrode and electrical connection can be inserted or removed. Whenever the cell is opened for changing or inspecting the reference or working electrode, or for introducing NH_4F, care is taken to exhaust nitrogen through the opening to prevent access of air or moisture to the HF in the cell.

A separate disposal system for fluorine was added to the apparatus as shown in Figure 4. The fluorine trap utilizes a bed of NaCl followed by a soda-lime mixture (1). Construction of the trap is shown in Figure 5.

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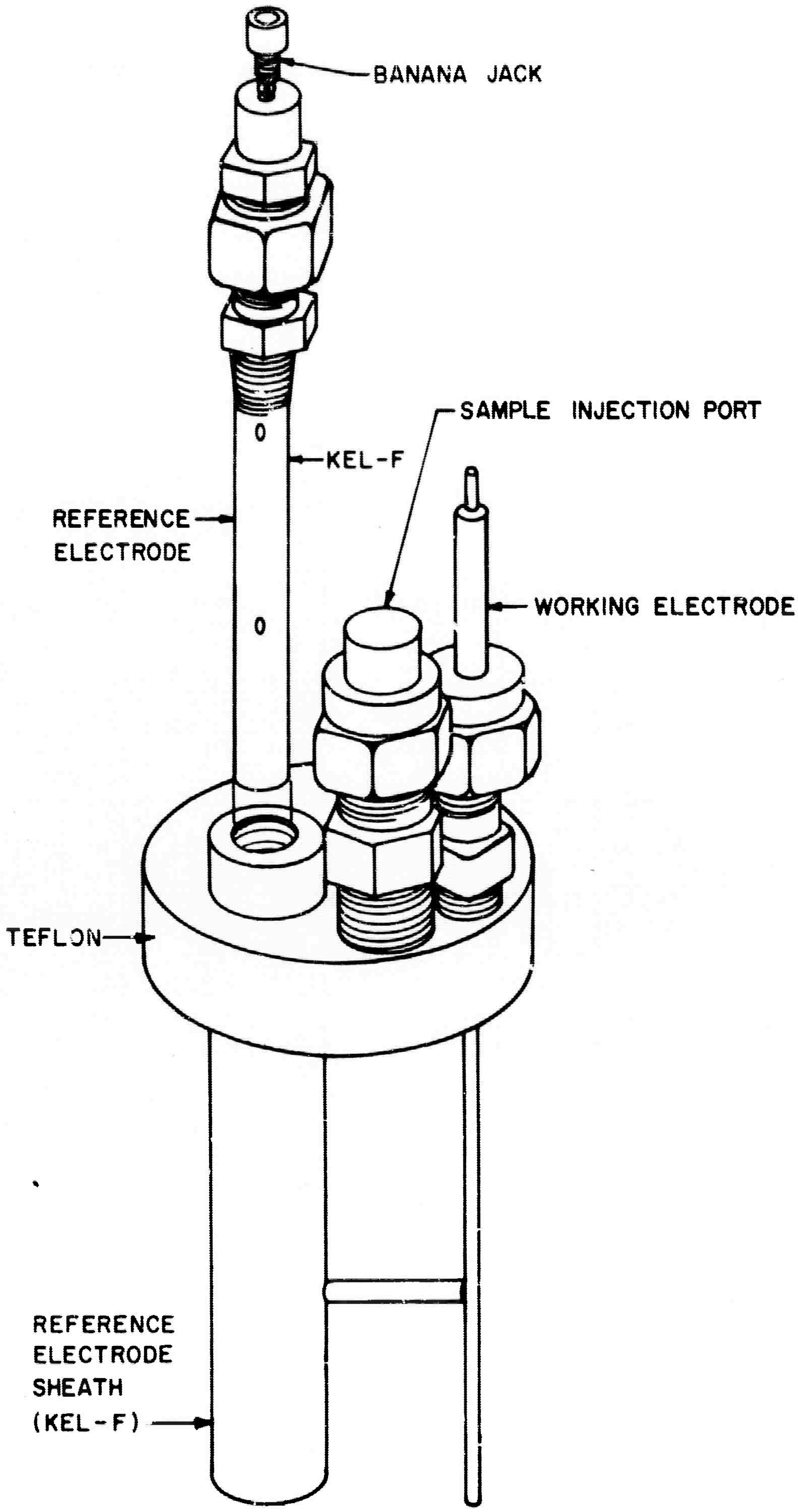

Fig. 3 - ELECTROLYTIC CELL LID

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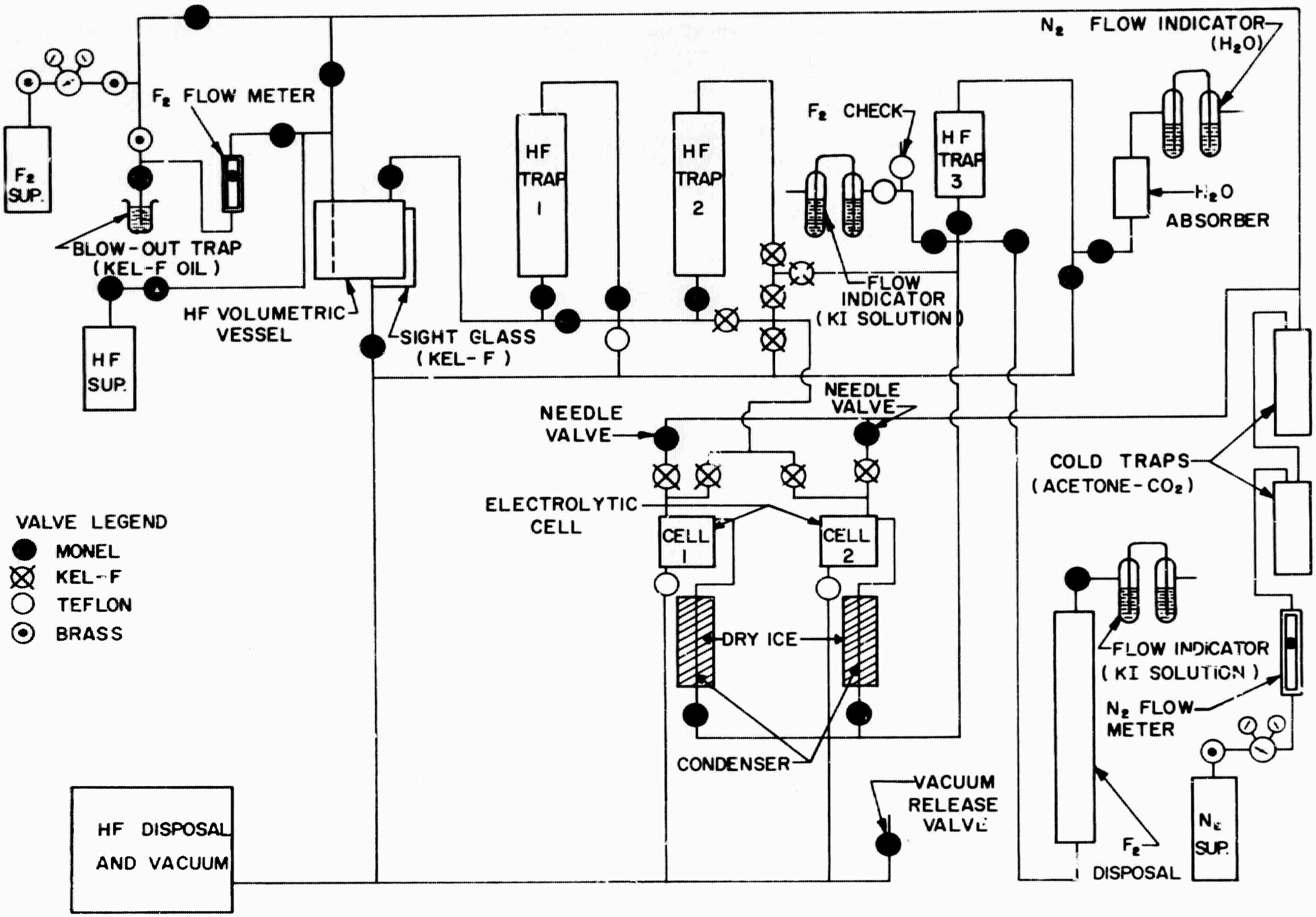

FIG. 4-HF HANDLING SYSTEM

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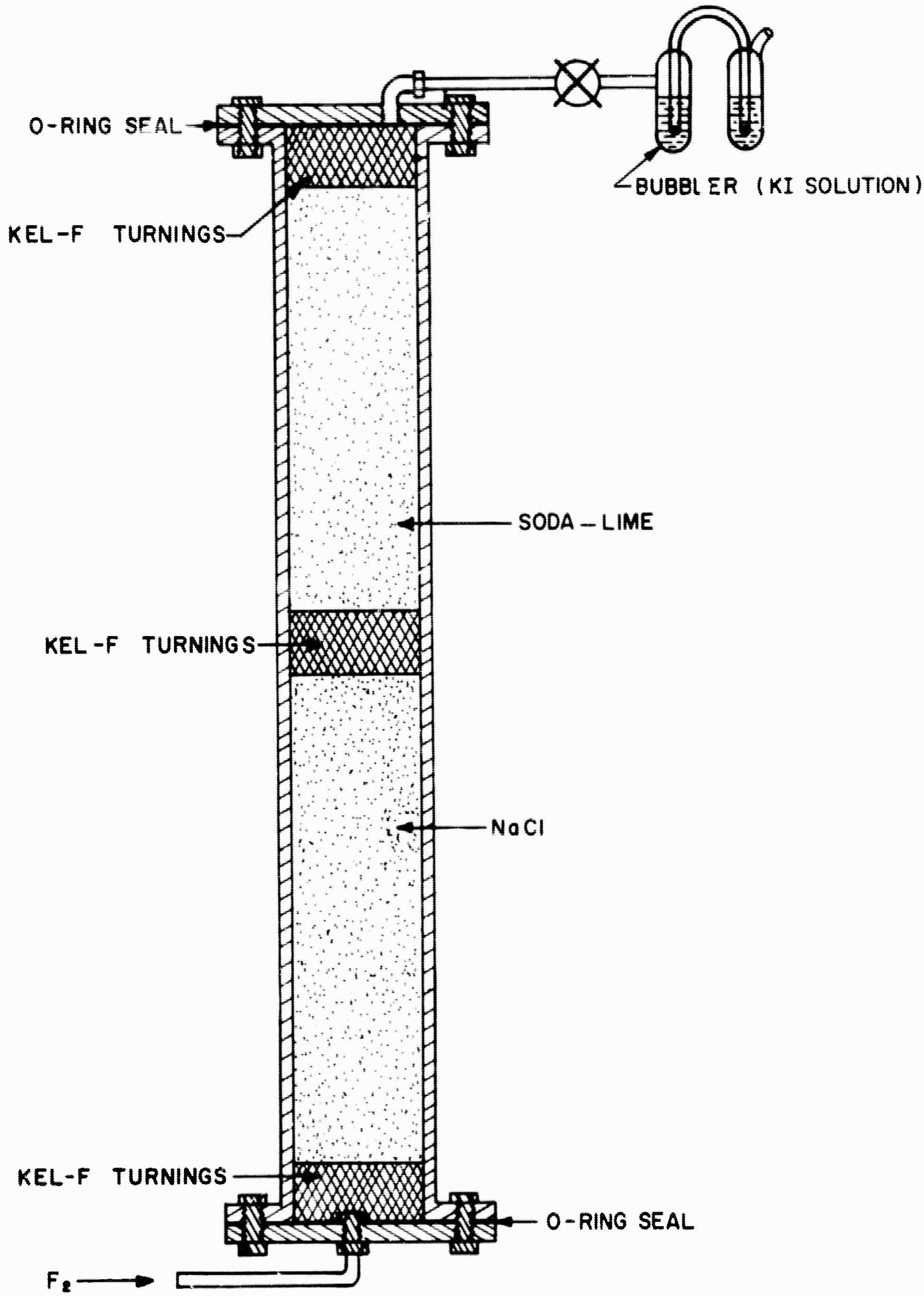

Fig. 5-FLUORINE DISPOSAL VESSEL

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III. ELECTROCHEMICAL FLUORINATION OF NH_4F IN ANHYDROUS HF WITH MONEL ANODES

In this quarter studies were made to determine if the electrochemical fluorination of NH_4F in anhydrous HF proceeded in a stepwise fashion as a function of potential. Anodic polarization curves of Monel electrodes were made in anhydrous HF containing various concentrations of NH_4F. Analytical grade NH_4F was dried to constant weight loss under vacuum over P_2O_5. Heat was not used on account of the volatility of NH_4F. A weighed injection device consisting of a Kel-F barrel and Teflon plunger was loaded with a small amount of NH_4F in a dry box and reweighed. The NH_4F was injected into the anhydrous HF in the electrolysis cell through an access port in the cell cover. Nitrogen gas maintained the cell at a positive pressure to prevent absorption of atmospheric moisture. Nitrogen was bubbled through the cell until the NH_4F dissolved, as indicated by attainment of constant resistivity. With the cell in a quiescent state, polarization curves were then obtained by use of an X-Y recorder and motor-driven potentiometer. Results of these experiments are shown in Figure 6 for anhydrous HF alone and also for various concentrations of added NH_4F. In these curves a plateau similar to a diffusion limited region consistently appeared at 3.0 to 5.0 volts. The current density on this plateau is independent of NH_4F concentration, or any contaminant added with the NH_4F. It is possible that the plateau is due to saturation of the protective fluoride coating on the electrode with fluorine. This adds a resistive barrier to the fluorine evolution reaction. The curves in Figure 6 are not corrected for IR drop through the HF solution, as this is small because of the short path to the reference electrode. The effects of concentration polarization with decreasing NH_4F concentration are clearly seen, however, no other evidence of depolarization of the electrode by addition of NH_4F was detected.

The effects of initial HF purity on the anodic polarization of Monel in HF solutions are shown in Figure 7. Pretreatment of

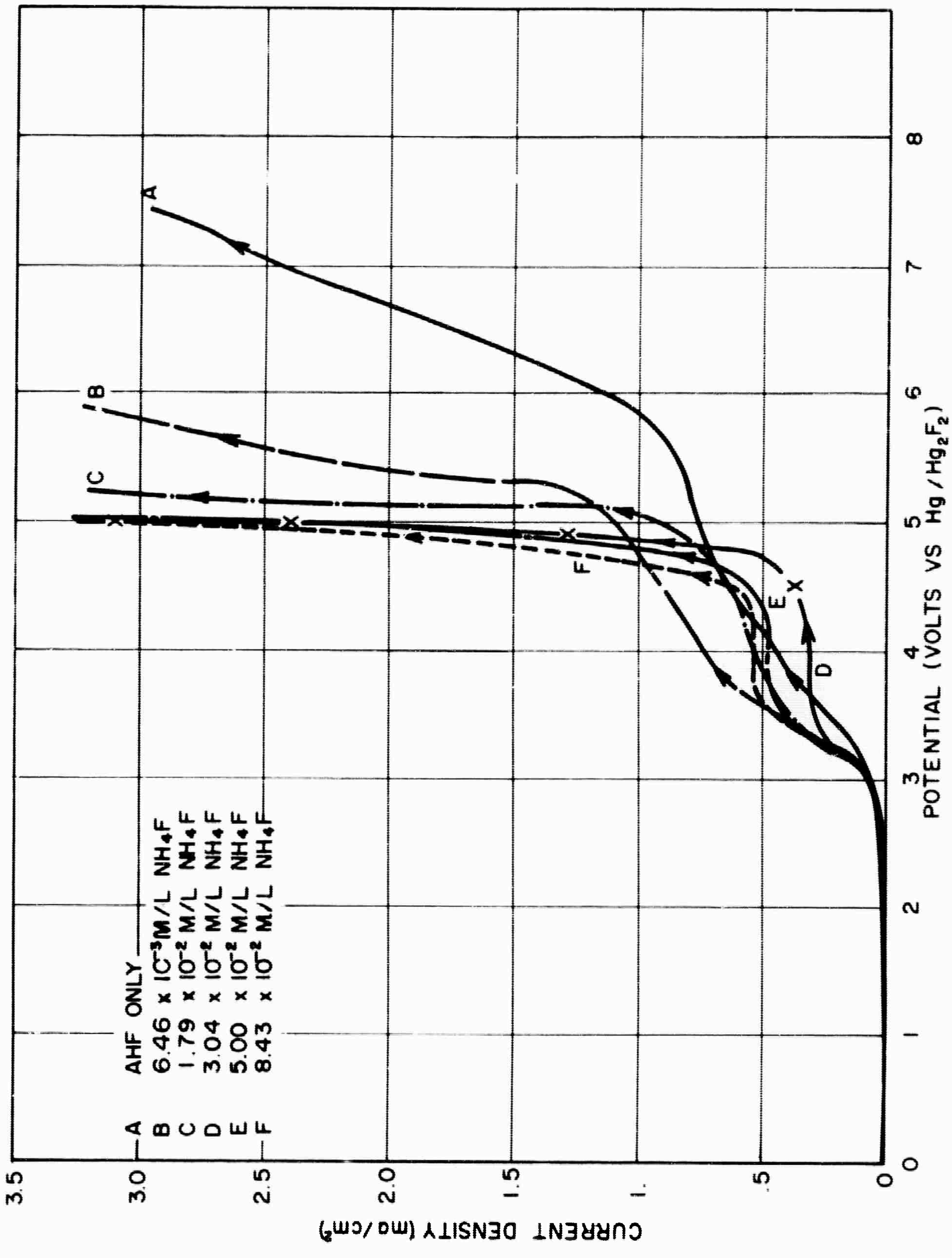

Fig. 6 - POLARIZATION CURVES FOR MONEL WITH NH_4F ADDED

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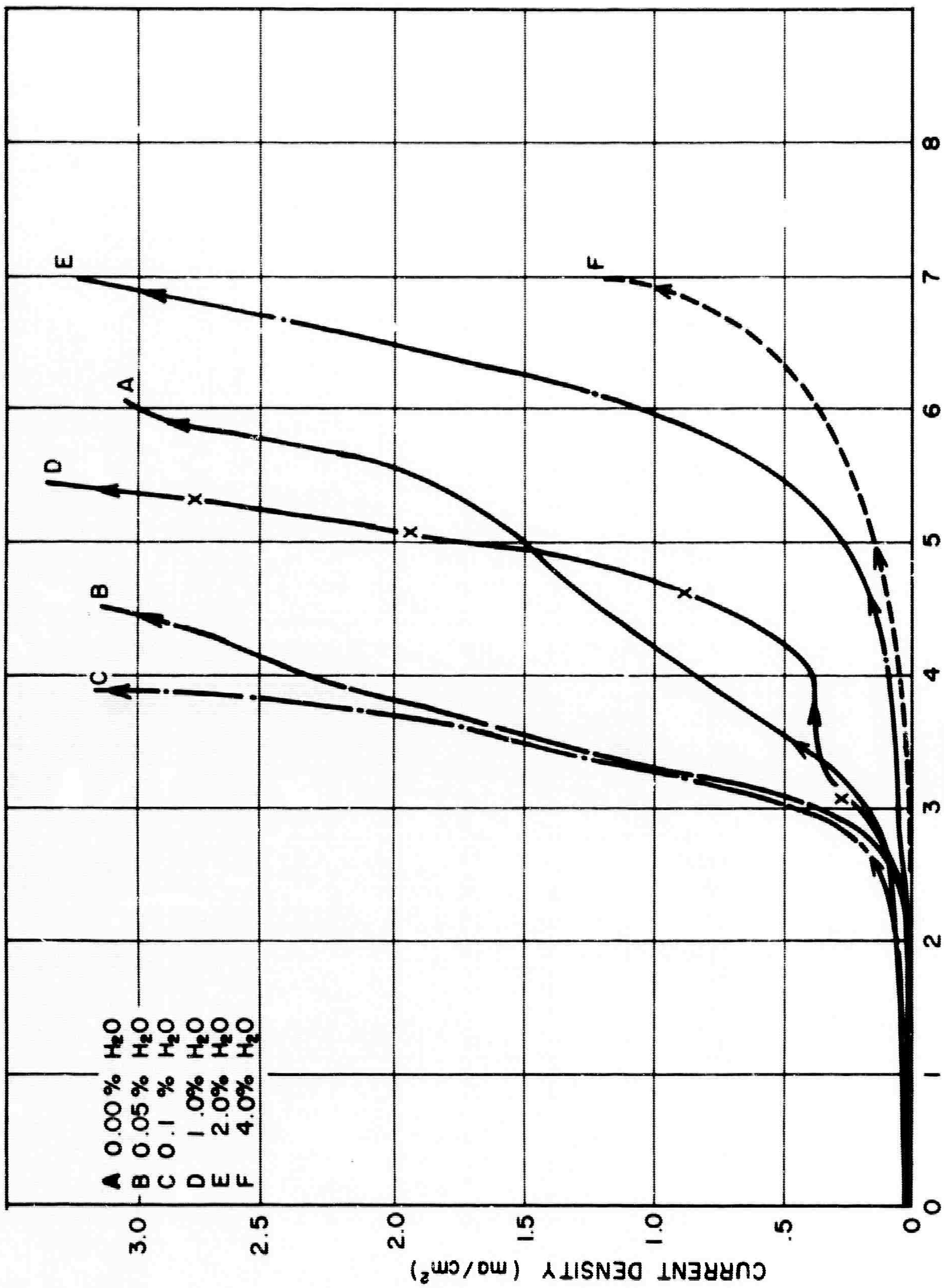

Fig. 7 -POLARIZATION CURVES FOR MONEL WITH WATER ADDED (% BY VOLUME)

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the Monel electrode in anhydrous HF produces a protective film on the electrode as evidenced by the passivity-type phenomenon shown in Figures 19 and 20 of Quarterly Status Report No. 5. Since completely anhydrous HF is difficult to prepare, it was of interest to determine the degree of effect of small amounts of water on the electrode behavior of Monel as an aid in interpreting polarization curves obtained in NH_4F solutions. As shown by Figure 7, the behavior of Monel anodes is highly dependent on the water content of liquid HF. Although the solution conductivity increases in proportion to the water content as shown in Figure 8, the potential required for fluorine evolution goes through a minimum at approximately 0.1% water. These results are interpreted as due to a change in composition and probably in resistivity of the film formed on the electrode surface.

Support for the conclusion that the diffusion limiting plateau observed in NH_4F solutions is due to the film composition on the electrode is given in Figure 9. On completion of an anodic polarization curve in NH_4F solution, sufficient water to give a 1% solution was added to the cell. The presence of water eliminated much of the plateau which indicates a change in film composition or depolarization by reaction of the water with a sorbed fluorine film.

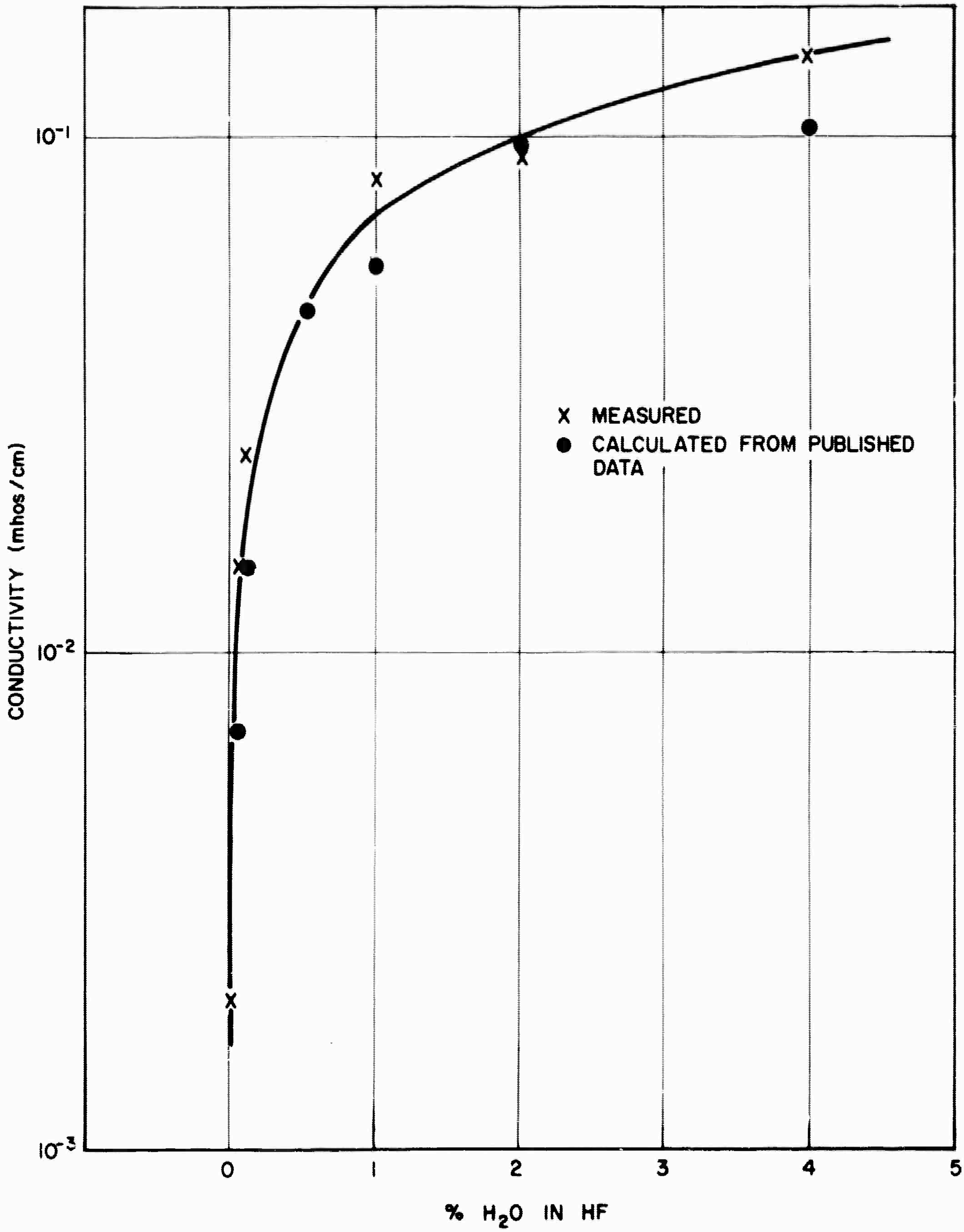

Fig. 8 - CONDUCTIVITY OF HF AS A FUNCTION OF H_2O CONCENTRATION

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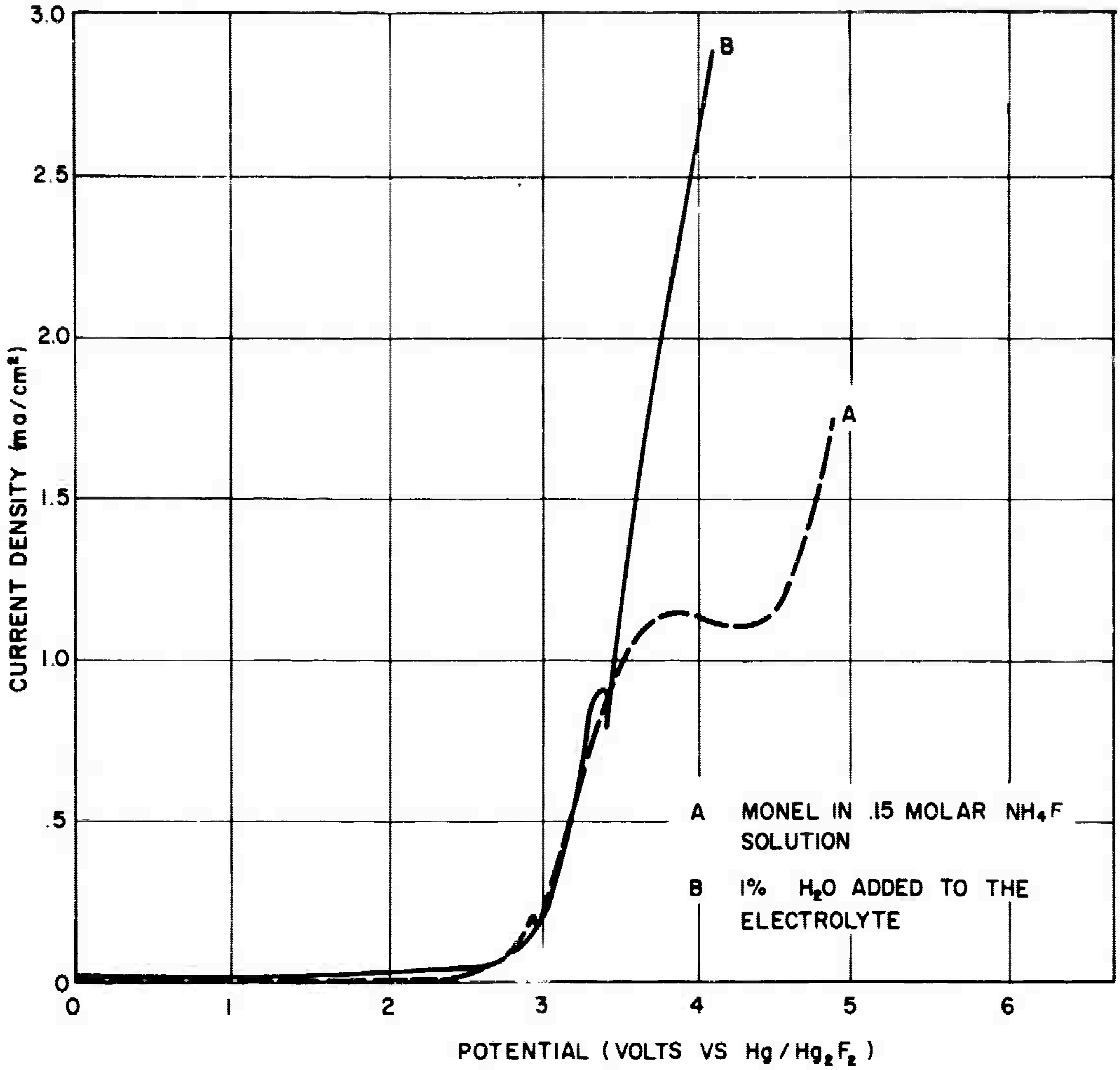

Fig. 9 - EFFECT OF H_2O ON THE POLARIZATION CURVE OF MONEL IN $HF + NH_4F$

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IV. HF CONDUCTIVITY

The maintenance of HF of high purity in the electrolysis cells is important in obtaining reproducible results and in interpreting the data obtained. In the past quarter several experiments were performed to determine if the carrier gas (N_2) might cause the conductivity of the AHF to increase due to any contaminant that escaped the purifying cold traps. The effects of helium gas, passed through a liquid nitrogen cold trap, were compared to nitrogen passed through a dry ice cold trap. Each gas was bubbled through the cell at a rate of 40 cc/min (twice the normal rate used) for 15 hours, while the conductivity of the HF was monitored by measurements with a pair of platinum electrodes. Both runs showed a decrease in resistivity of approximately 250 Ω-cm but returned to their initial values of approximately 4000 Ω-cm after the gas was shut off and the cell allowed to return to its equilibrium temperature of -20°C. The values recorded for these two runs are shown in Figure 10. Thus we have concluded that any increase in the conductivity was due only to a slight temperature increase caused by the warmer nitrogen or helium gas bubbled through the electrolytic cell. The cell temperature returned to its equilibrium temperature slowly due to the poor thermal conductivity of Kel-F.

The conductivity of the AHF in the new Kel-F electrolytic cells was checked for periods up to 15 hours, with the cell closed off, to determine if there was any water diffusion through the cell wall. The initial resistivity for these runs was about 9000 Ω-cm in each case. The results showed a maximum decrease of 190 Ω-cm for a 15-hour period. Ukaji and Kageyama (2) developed an empirical equation relating the H_2O content of AHF to its resistivity as follows:

$$\log x = 1.808 - 1.528 \log R$$

where

R = resistivity $\qquad$ x = % H_2O by weight.

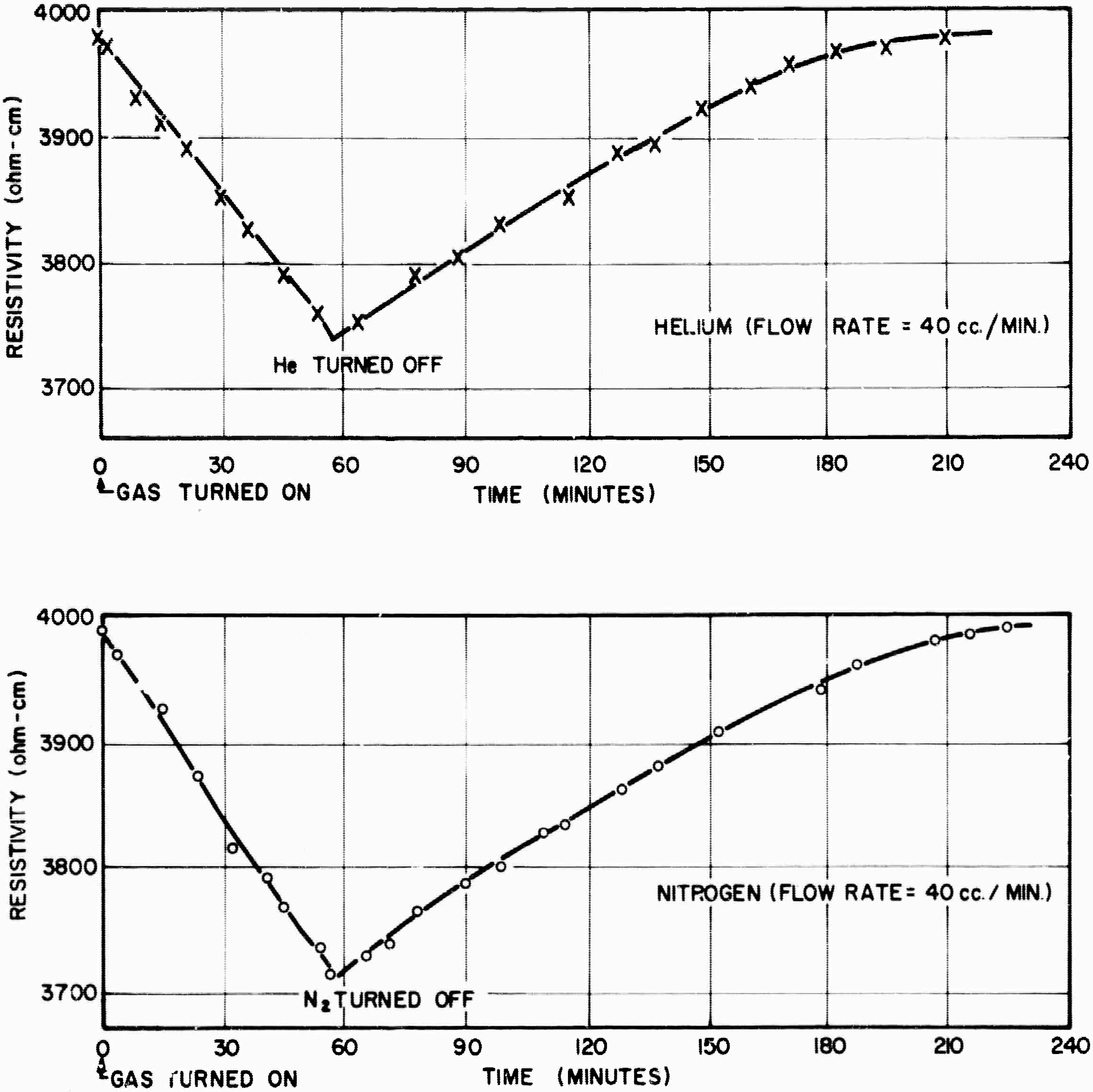

Fig. 10-EFFECTS OF N_2 AND He ON THE RESISTIVITY OF THE AHF

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Using this equation, a diffusion rate of 1.73×10^{-7} ml/hr can be calculated as a result of the 190 Ω-cm decrease in resistivity. Thus any water diffusion during a normal working day is negligible. This will allow more accurate interpretations of conductivity changes in the electrolytic cells.

It has not been possible with the apparatus employed here to obtain HF with a conductivity less than 10^{-2} mho/cm by the trapping procedure employed; therefore, the trapping procedure has been supplemented by pre-electrolysis in the cells. By electrolyzing the HF in the electrolytic cells before it is used, very pure AHF was obtained. One example of this is that the resistivity of the HF increased from 300 to 8000 Ω-cm after a potential of 7.0 volts and a current of 18 ma was applied across the nickel screens for 15 hours. Periods of approximately 20 hours are needed to get a resistivity of greater than 10^4 Ω-cm. According to Ukaji and Kageyama's equation (2) this corresponds to 5×10^{-5} ml of water present in the electrolytic cell, which contains 100 ml of AHF.

When a clean Monel electrode was introduced into the cell, the conductivity increased by at least a factor of two. This was presumably due to metal ion contamination on corrosion of the Monel in the AHF. When the first rapid polarization curve was run on a Monel electrode after it had been in the cell for 100 minutes, the resistivity decreased an additional amount from 2900 to 2710 Ω-cm.

The addition of small amounts of water or NH_4F to AHF had similar effects on the resistivity of the AHF. Eight milligrams (2.16×10^{-3} M/l) of NH_4F were added to the AHF and the resistivity decreased from 8000 to 45 Ω-cm. When 0.05% water was added to AHF, the resistivity decreased from 6000 to 68 Ω-cm. From these data the equivalent conductance of water in HF was calculated to be 528 and 447 mhos-cm^2 for 0.05 and 0.1%, respectively. These are similar to values obtained for solutions of strong acids in water.

V. WORKING ELECTRODES

A. Monel

Monel is the best material for working anodes in HF found to date in this work. It has been found to exhibit a passivity-type electrode behavior in HF and corrodes at only an extremely low rate under anodic bias; consequently, it is the preferred electrode material for studies of the electrochemical fluorination of HF.

It is planned to study the products of NH_4F fluorination by cathodic reduction in electrolyzed solutions; therefore, the behavior of the working electrode alone on cathodic reduction from controlled anodic potential bias is important in this work. A Monel electrode was held at a fixed anodic potential in anhydrous HF until the current density was constant. Then, at time t = 0, the anodic bias was switched out and a constant cathodic current of 1.0 ua/cm^2 was applied to reduce the film from the electrode. Potentials were recorded as a function of time until the potential became constant as shown in Figure 11. The amount of charge passed was calculated for each reduction and found to be:

146 ucoul/cm^2 for 2.0 v
150 ucoul/cm^2 for 3.0 v
650 ucoul/cm^2 for 4.0 v
640 ucoul/cm^2 for 5.0 v
575 ucoul/cm^2 for 6.0 v

Assuming a roughness factor of unity and formation of NiF_2 and CuF_2 in the ratio of the metals in Monel (66% Ni and 31.5% Cu) (3), 300 ucoul/cm^2 corresponds to a monolayer of film.

Thus, it appears that there is about half a monolayer of film on the electrode until the fluorine evolution potential is exceeded, after which the film thickness is approximately two monolayers. There exists the possibility that the product reduced at lower anodic potentials is a protective fluoride while

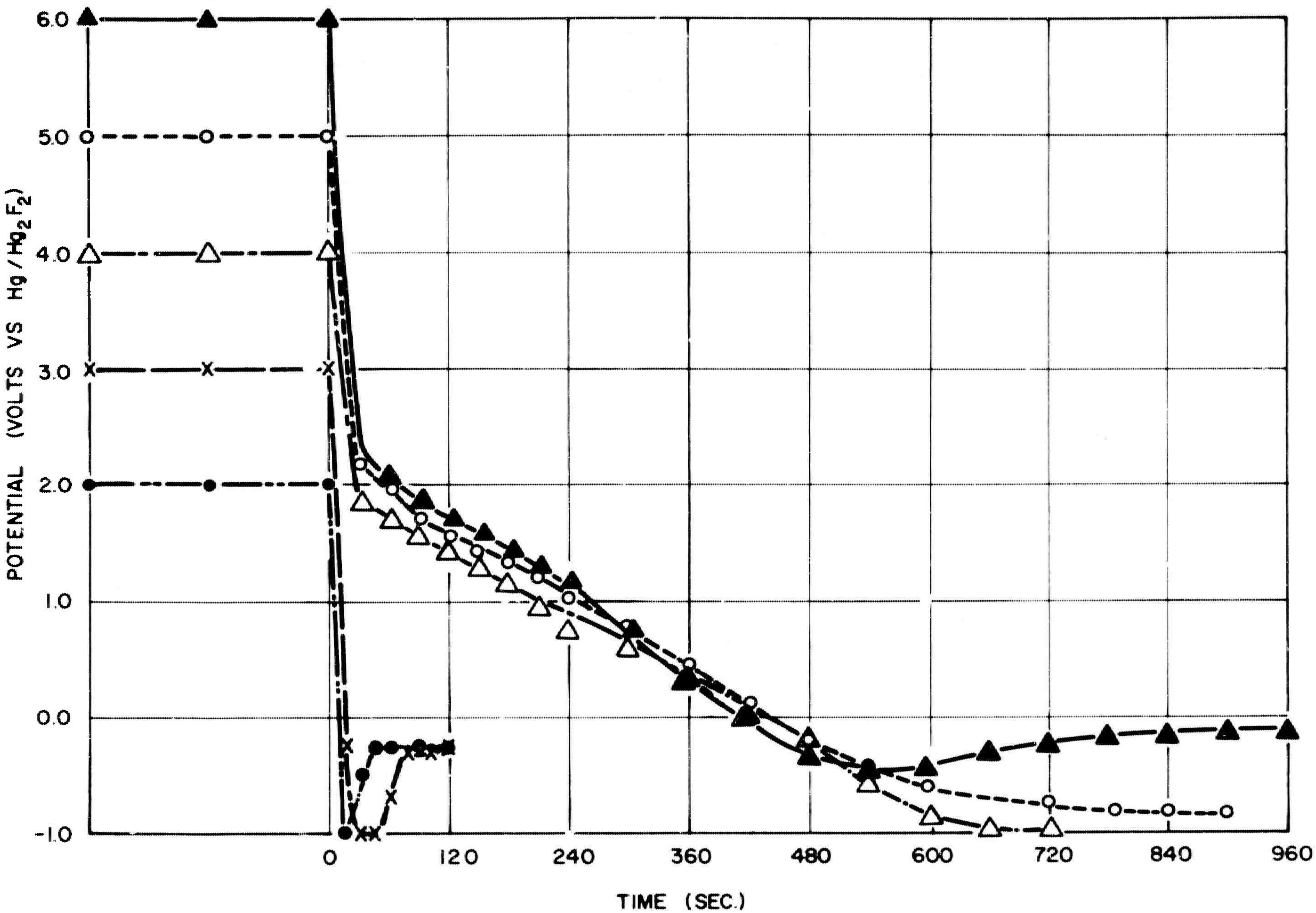

Fig. 11 - CATHODIC STRIPPING OF MONEL IN AHF

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the products reduced at higher anodic potentials consists of protective fluoride saturated with fluorine. The existence of a fluorine film is indicated by the beginning of a potential arrest at +2.0 volts as shown in Figure 11 which is approximately the fluroine evolution potential observed on most electrode materials. If this is correct, then an additional polarization component is introduced at higher anodic potentials by a change in film composition. Attempts to solve this problem by measurement of electrode film resistance are in progress.

B. Pyrolytic Carbon

Pyrolytic carbon disks were sealed in Kel-F so that only the surface of the carbon lamella was exposed to the AHF (see Figure 12). It was hoped that exposure of onlv one plane of the pyrolytic layer structure would prevent the disintegration observed by other workers. Electrical contact was made by sealing a Teflon-coated nickel wire to the back side of the carbon electrode.

Anodic polarization caused exfoliation of the layers of the electrode. An electrode which was immersed only in HF at open circuit showed no signs of corrosion or exfoliation as seen in Figure 12. Thus, it is concluded that, although pyrolytic carbon is resistant to HF, fluorine penetrates the lattice and causes disintegration of the structure. No further experimental work with pyrolytic carbon is planned.

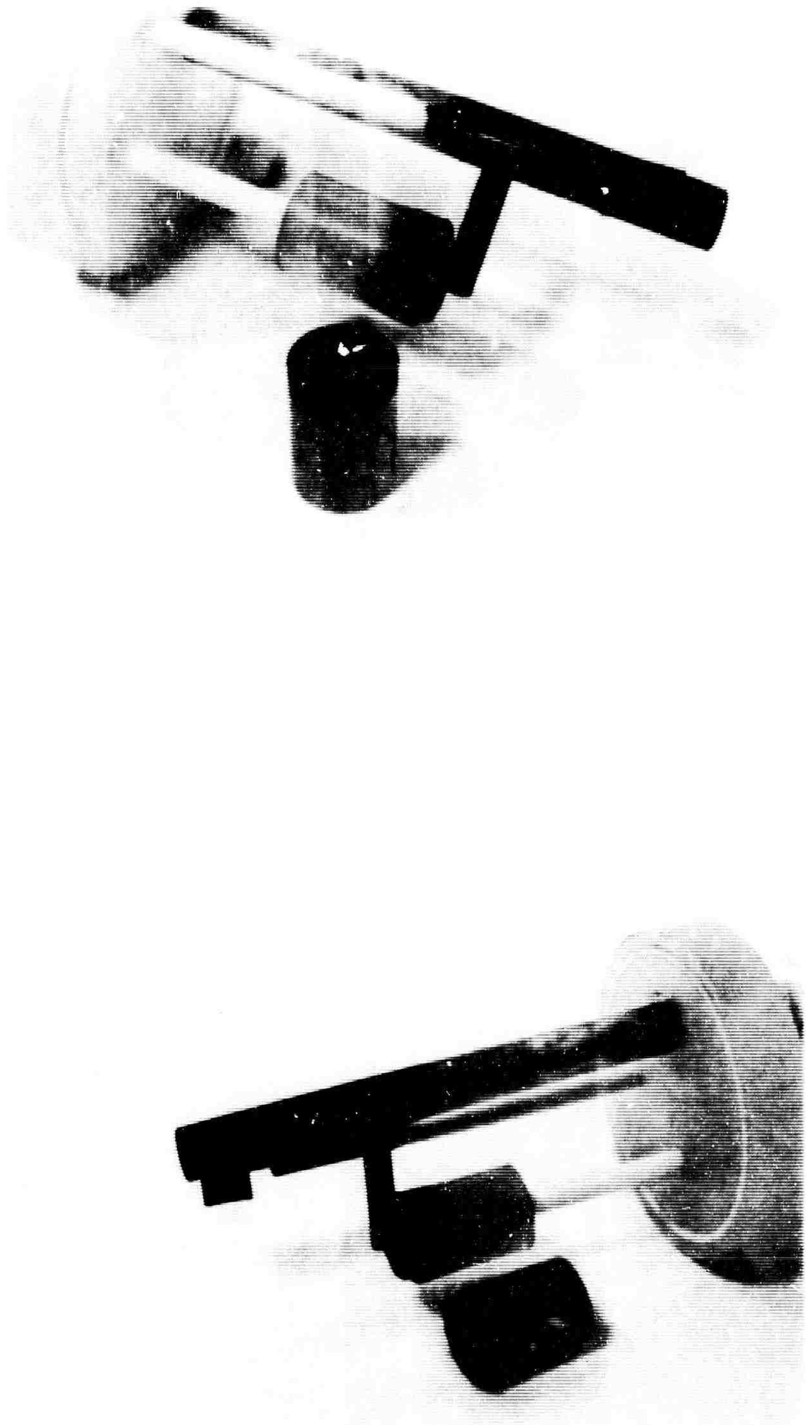

Fig. 12 - PYROLYTIC CARBON ELECTRODES

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VI. DISCUSSION

It appears from the polarization curves of Monel in AHF solutions of NH_4F that the fluorination of NH_3 proceeds by chemical reaction rather chan by an electrochemical mechanism. This is indicated by the lack of any NH_4F dependent wave or peak in the anodic polarization curves.

The peak or plateau noticed in some of our anodic polarization curves on Monel in AHF (with or without H_2O or NH_4F) may be due to the formation of a secondary type of film or change in the character of the film. Further studies on this are under way.

The polarization curves for the electrochemical fluorination of NH_4^+ ions will be studied further with the view of identifying the products obtained under constant potential electrolysis. If NH_4^+ is fluorinated in random rather than stepwise fashion, it is still possible to obtain workable concentrations of partially fluroinated cations by control of the fluorine evolution rate and diffusion of NH_4^+ ions to the electrode. Also, a more accurate examination of electrode behavior in the potential range of +2.0 to +4.0 volts vs Hg/Hg_2F_2 is now possible due to clarification of the change in film structure of Monel at higher anodic potentials.

It is now possible to prepare and maintain AHF of high purity for long periods of time in the electrolysis cells of current design using a combined trapping and pre-electrolysis procedure for purification of the HF. These results and better knowledge of electrode behavior in HF have aided greatly in interpreting the experimental data which have been obtained.

VII. FUTURE WORK

Work now in progress consists of polarization studies using Monel as the working electrode with NH_4F and N_2H_4 added to the AHF.

Fluorine resistant gas and liquid IR cells have been obtained and will be used in taking the IR spectra of samples taken from the electrolytic cells under various conditions. Successful application of these spectra should aid in determining the identity of products obtained by the electrochemical fluorination of NH_3 and N_2H_4 in AHF.

Studies on the behavior of electrode materials will also be continued.

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